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Nowe sole starczanów pochodnych 1,3-dioksanów I sposób ich wytwarzania

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**NEW SULFATE SALTS OF DERIVATIVES OF 1,3-DIOXANES,
AND METHOD FOR THEIR PRODUCTION**

P a t e n t C l a i m s

1. New sulfate salts of derivatives of 1,3-dioxanes, having the names of cis- and trans-2-alkyl-5-hydroxy-1,3-dioxanes and generalized formulae, diagrammatically represented in the drawings by means of formulae 1 and 2, respectively, in which **n** amounts from 7 to 13, **m** amounts to 1 or 2, **X** constitutes a cation of a metal of the first or second group of the periodic table of chemical elements, such a lithium, potassium, cesium, magnesium, calcium, or barium,

ammonium cation, or pyridine cation.

2. Method for the production of new sulfate salts of derivatives of cis- and/or trans-2-alkyl-hydroxy-1,3-dioxanes, having generalized formulae 1 and 2, respectively, in which **n** amounts from 7 to 13, **m** amounts to 1 or 2, **X** constitutes a cation of a metal of the first or second group of the periodic table of chemical elements, such a lithium, potassium, cesium, magnesium, calcium, or barium, ammonium cation, or pyridine cation **characterized in that** cis- and/or trans-2-alkyl-5-hydroxy-1,3-dioxanes, having generalized formulae 3 and/or 4, in which **n** has the aforementioned value, are subjected to reaction with chlorosulfuric acid in a solution of a solvent, obtained in the form of carbon tetrachloride with the addition of pyridine, whereupon the solvent is evaporated while the residue is purified, or is introduced into an alcohol-water solution, or a suspension of a hydroxide, a carbonate, or a bicarbonate of a metal of the first or second group of the periodic table of chemical elements, defined above, or of ammonium hydroxide, while the solvent is evaporated, and the residue is purified.

3. Method as claimed in claim 2, **characterized in that** the molar ratio of the derivative or the mixture of derivatives of 1,3-dioxane to the chlorosulfuric acid and to the pyridine is confined within the range of 1 : 1.1 : 2.3 to 1 : 1.2 : 2.5.

4. Method for the production of new sulfate salts of derivatives of cis- and/or trans-2-alkyl-5-hydroxy-1,3-dioxanes, having generalized formulae 1 and 2, respectively, in which **n** amounts from 7 to 13, **m** amounts to 1 or 2, **X** constitutes a cation of a metal of the first or second group of the periodic table of chemical elements, such a lithium, potassium, cesium, magnesium, calcium, or barium, ammonium cation, or pyridine cation **characterized in that** cis- and/or trans-2-alkyl-5-hydroxy-1,3-dioxanes, having generalized formulae 3 and/or 4, in

which **n** has the aforementioned value, are subjected to reaction - in a solution of a solvent, produced in the form of carbon tetrachloride - with sulfur trioxide, obtained in the form of the pyridine-sulfur trioxide complex, whereupon the solvent is evaporated while the residue is purified, or the is introduced to an alcohol-water solution, or suspension of a hydroxide, a carbonate, or a bicarbonate of a metal of the first or second group of the periodic table of the chemical elements, defined above, or of ammonium hydroxide, while the solvent is evaporated, and the residue is purified.

5. Method as claimed in claim 4, **characterized in that** the molar ratio of the derivative or the mixture of derivatives of 1,3-dioxane to the pyridine sulfur trioxide complex is confined within the range of 1 : 1.1 to 1 : 1.2

Object of the invention are new sulfate salts of derivatives of 1,3 dioxanes, having the names of cis- and trans-2-alkyl-5hydroxy-1,3-dioxanes, having generalized formulae 1 and 2 -, which are diagrammatically represented in the drawing, and in which **n** amounts from 7 to 13, **m** amounts to 1 or 2, **X** constitutes a cation of a metal of the first or second group of the periodic table of chemical elements, such as lithium, potassium, cesium, magnesium, calcium, or barium, an ammonium cation, or a pyridine cation.

The new salts exhibit a surface activity along the interphase interfaces , and are intended to be individually used as active ingredients, detergents, wetting agents, hydrotropes, swelling agents, anti-foaming agents, emulsifying agents, washing agents, deflocculating agents, either individually, or in mixtures with other surface acting substances (surfactants), in manufactured articles of household chemistry, textile industry, lube oils, lubricants, and other auxiliary agents.

Alkyl sulfates, furnished as a result of the reaction of sulfatizing of long-chained aliphatic alcohols, or within the framework of the reaction of addition of sulfuric acid to unsaturated hydrocarbons, and subsequent neutralization of the alkyl sulfuric acids [alkyl hydrogen sulfates] thus formed, generally speaking by means of available hydroxides, carbonates, or gaseous ammonia, constitute one of the most important groups of anionic surface active compounds, having multifarious practical applications, described in the monograph by W M. Linfield (Ed.), Anionic Surfactants, Part I and II, M. Dekker, Inc., New York, N.Y. USA, 1976. From the US Pat. NO. 3,909,460 and No. 3,948,953, there are known ammonium salts of sulfates, produced from five-member cyclic acetals, 2-mono-substituted or 2,2-di-substituted 4-hydroxymethyl-1,3-dioxanes, used as hydrophobic semifinished products. Form the Polish patent specification No. 162, 441, there is known a method for the production of surface-active sodium sulfates, furnished from 6-member cyclic acetals, 2,5-di-substituted, or 2,2,5-tri-substituted 5-hydroxymethyl-1,3-dioxanes, employed as hydrophobic semifinished products.

Sulfate salts of derivatives of 1,3-dioxanes, having the names of cis- and trans-2-alkyl-5-hydroxy-1,3-dioxanes and generalized formulae, diagrammatically represented in the drawings by means of formulae 1 and 2, respectively, in which **n** amounts from 7 to 13, **m** amounts to 1 or 2, **X** constitutes a cation of a metal of the first or second group of the periodic table of chemical elements, such a lithium, potassium, cesium, magnesium, calcium, or barium, ammonium cation, or pyridine cation, are not known.

The invention pertains to new sulfate salts of derivatives of 1,3-dioxanes, having the names of cis- and trans-2-alkyl-5-hydroxy-1,3-dioxanes, and having generalized formulae, diagrammatically represented in the drawings by means of formulae 1 and 2, respectively, in

which **n** amounts from 7 to 13, **m** amounts to 1 or 2, **X** constitutes a cation of a metal of the first or second group of the periodic table of chemical elements, such a lithium, potassium, cesium, magnesium, calcium, or barium, ammonium cation NH_4^+ , or pyridine cation, $\text{C}_5\text{H}_5\text{NH}^+$.

The invention also pertains to a method for the production of new sulfate salts of derivatives of cis- and trans 2-alkyl-5-hydroxy-1,3-dioxanes, having generalized formulae 1 and 2, respectively, in which **n** amounts from 7 to 13, **m** amounts to 1 or 2, **X** constitutes a cation of a metal of the first or second group of the periodic table of chemical elements, such a lithium, potassium, cesium, magnesium, calcium, or barium, ammonium cation NH_4^+ , or pyridine cation, $\text{C}_5\text{H}_5\text{NH}^+$.

The essence of the invention is based on the fact that cis- and/or trans-2-alkyl-5-hydroxy-1,3-dioxanes, having generalized formulae 3 and 4, respectively, in which **n** has the aforementioned value, are subjected to reaction with chlorosulfuric acid, in a solution of a solvent, obtained in the form of carbon tetrachloride, with the addition of pyridine, whereupon the solvent is evaporated, and the residue is subjected to purification, or the residue is introduced to an alcohol-water solution, or a suspension of hydroxide, carbonate, or bicarbonate of a metal of the first or the second group of the periodic table of chemical elements, such as lithium potassium, cesium, magnesium, calcium, or barium, or ammonium hydroxide, the solvent is evaporated, and the residue is purified. It is advantageous when the molar ratio of the derivative or the mixture of derivatives of 1,3-dioxane to the chlorosulfuric acid and to the pyridine is confined within the range of 1 : 1.1 : 2.3 to 1 : 1.2 : 2.5.

The essence of the invention is also based on the fact that cis- and/or trans-2-alkyl-5-hydroxy-1,3 dioxanes, having generalized formulae 3 and 4, respectively, in which **n** has the

aforementioned value, are subjected - in a solution of a solvent, furnished in the form of carbon tetrachloride - to reaction with sulfur trioxide, produced in the form of pyridine - sulfur trioxide complex, whereupon the solvent is evaporated, and the residue is purified, or the residue is introduced into an alcohol-water solution, or a suspension of a hydroxide, a carbonate, or a bicarbonate of a metal of the first or second group of the periodic table of chemical elements, such as lithium, potassium, cesium, magnesium, calcium, or barium, or of ammonium hydroxide, whereas the solvent is evaporated, and the residue is purified. It is advantageous when the molar ration of the derivative or derivatives of 1,3-dioxane to the pyridine sulfur trioxide complex is confined within the limits of 1 : 1.1 to 1 : 1.2.

The principal advantages of the invention are the production of anionic surfactants, having a high surface activity, stability of the sulfates produced in neutral medium, as well as their susceptibility to hydrolysis in acid medium to products, which do not exhibit surface activity, as a result of which the sulfates thus produced are not to any considerable extent deleterious to the environment.

The principal advantages of the method in accordance with the invention also consist in that the semifinished hydrophobic products are easily available, in particular from quaternary mixtures of cis- and trans-2-alkyl-5-hydroxy-1,3 dioxanes as well as cis- and trans- 2-alkyl-4-hydroxymethyl-1,3 dioxanes, and also in that the reaction of sulfatizing can easily be carried out, and in that the sulfate salts can easily be extracted, as well as in that it is possible to obtain compounds, having a specified geometric structure.

The objective of the invention is attained in accordance with the examples, cited below, within the framework of the chemical reactions, diagrammatically represented in the drawings 1

thru 3.

E x a m p l e I.

To a solution of 0.010 kg, i.e. 0.0387 moles, of a mixture of cis- and trans-2-undecyl-5-hydroxy-1,3-dioxanes in 0.070 dm³ of dried carbon tetrachloride in 2×10^{-3} dm³ of dried pyridine, there are introduced - over the course of vigorous agitation, at room temperature - in several batches, 7.4×10^{-3} kg, i.e. 0.0464 moles, of pyridine sulfur trioxide complex. The thorough mixing continues at the same temperature for a period of 1 hour, while the next thorough agitation is carried out at a temperature of 310 K for a period of 6 to 8 hours. After the evaporation of the solvent and the crystallization of the residue from ethyl alcohol has taken place, there are produced 0.0127 kg, i.e. 89%- mole of a mixture of surface active pyridine sulfate salts of derivatives of cis- and trans-2-undecyl-5-hydroxy-1,3-dioxanes, having the generalized formulae 1 and 2, in which **n** amounts to 11, **m** amounts to 1, **X** constitutes the pyridine cation H₅N₅H⁺. Empiric formula: C₂₀H₃₅NO₆S. Contents: C, H, S, N, calculated: 57.53, 8.45, 7.68, 3.35% by weight, respectively. Contents, determined: 57.60, 8.5, 7.7, 3.3 % by weight, respectively. Melting point: 372 to 376 K. Krafft point for 1 % by weight of aqueous solution is lower than 293 K.

E x a m p l e II.

To a solution of 0.010 kg, i.e. 0.0387 moles, of a mixture of cis- and trans-2-undecyl-5-hydroxy-1,3-dioxanes in 0.070 dm³ of dried carbon tetrachloride in 8×10^{-3} dm³ of dried pyridine, there are introduced dropwise at a temperature of 280 to 285 K, while thorough agitation takes place for a period of 0.5 hours, 5.4×10^{-3} kg, i.e. 0.46 moles of chlorosulfuric acid. After the entire amount of chlorosulfuric acid has been added dropwise, the mixing continues for 1 hour at room

temperature while the subsequent mixing or agitation is carried out for 6 to 8 hours at a temperature of about 310 K. After the solvent has been evaporated, the residue is gradually introduced at room temperature to a suspension of 3.7×10^{-3} kg, i.e. 0.05 moles of calcium hydroxide in 0.15 dm³ of water. After the water has evaporated, and the residue crystallizes from ethyl alcohol, there are produced 0.012 kg, i.e. 86.5 %-mol of a mixture of calcium sulfate salts of derivatives of cis- and trans-2-undecyl-5-hydroxy-1,3-dioxanes, having a generalized formulae 1 and 2, in which **n** amounts to 11, **m** amounts to 2, **X** constitutes a calcium cation. Empiric formula: C₃₀H₅₈O₁₂S₂Ca; calculated contents of C, H, S, respectively, 50.40, 8.18, 8.97% by weight; contents, determined: 50.3, 8.1, 8.8% by weight, respectively; melting point higher than 533 K. Krafft point higher than 370 K. The mixture of surface-active magnesium sulfate salts of derivatives of cis- and trans-2-undecyl-5-hydroxy-1,3-dioxanes, having generalized formulae 1 and 2, in which in which **n** amounts to 11, **m** amounts to 2, **X** constitutes a magnesium cation Mg (85% mol yield) possesses the following characteristics: empiric formula: C₃₀H₅₈O₁₂S₂Mg; calculated contents of C, H, S: 51.53, 8.36, 9.17 % by weight, respectively; contents determined: 51.6, 8.4, 9.2 % by weight, respectively; melting point (decomposition) is higher than 540 K; Krafft point for 1 % by weight of aqueous solution is lower than 293 K. The mixture of surface active barium sulfate salt of derivatives of cis- and trans-2-heptyl-5hydroxy-1,3-dioxanes, having generalized formulae 1 and 2, in which **n** amounts to 7, **m** amounts to 2, **X** constitutes the barium cation (85% mol yield) possesses the following characteristics: empiric formula C₂₂H₄₂O₁₂S₂Ba; calculated contents of C, H, S 37.75, 6.05, 9.16 % by weight respectively; contents determined: C, H, S 37.8, 6.0, 9.0, respectively; melting point: higher than 540 K; Krafft point for a 1% by weight of aqueous solution: 345 K.

E x a m p l e III

The product of the reaction of the mixture of cis- and trans-2-undecyl-5-hydroxy-1,3-dioxanes with the pyridine sulfur trioxide complex, as cited in Example I, is gradually introduced - after the evaporation of the solvent - into 0.15 dm³ of an alcohol-water solution of ammonium hydroxide, containing 0.1 moles of NH₃. After the evaporation of the excess amount of ammonium After the evaporation of the ammonium as well as the solvents and the crystallization of the residue form ethyl alcohol, there are produced 0.0114 kg , i.e. 83%-mol of a mixture of surface-active ammonium sulfate salts of the derivative of cis- and trans-2-undecyl-5-hydroxy-1,3-dioxanes, having generalized formulae 1 and 2, in which in which **n** amounts to 11, **m** amounts to 1, **X** constitutes the ammonium cation NH₄⁺. Empiric formula C₁₅H₃₃NO₆S, calculated contents of C, H, N, S: 50.68, 9.36, 3.94, 9.02 % by weight; contents, determined: 50.8, 9.5, 3.9, 9.1 % by weight, respectively; melting point: 416 - 418 K; Krafft point of the product for 1% by weight of an aqueous solution is 302 K.

E x a m p l e IV.

To a solution of 0.010 kg, i.e. 0.0387 moles, of a mixture of cis- and trans-2-undecyl-5-hydroxy-1,3-dioxanes in 0.070 dm³ of dried carbon tetrachloride in 2*10⁻³ dm³ of dried pyridine, there are introduced - over the course of vigorous agitation, at room temperature - in several batches, 7.4*10⁻³ kg , i.e. 0.0464 moles, of the pyridine sulfur trioxide complex. The thorough mixing continues at the same temperature for a period of 1 hour, while the next thorough agitation is carried out at a temperature of 310 K for a period of 6 to 8 hours. After the evaporation of the solvent, the residue is gradually introduced at room temperature to a suspension of 7.2*10⁻³ kg, i.e. 0.045 moles of potassium carbonate in 0.1 dm³ of a mixture of

solvents, ethyl alcohol- water (3:1, v/v). After the evaporation of the solvents and the crystallization of the residue from the ethyl alcohol, there are furnished 0.0136 kg, i.e. 93 %-mol of surface-active potassium salt of the sulfate [potassium-sulfate salt] of the derivative of cis-2-undecyl-5-hydroxy-1,3-dioxane, having generalized formula 1, in which $n = 11$, $m = 1$, X constitutes the potassium anion K. Empiric formula: $C_{15}H_{29}O_6SK$; calculated contents of C, H, S 47.84, 7.76, 8.52 % by weight, respectively; determined contents: 47.9, 7.6, 8.3 % by weight; melting point (decomposition) 473-475 K; Krafft point for 1% by weight of an aqueous solution: 315 K. The surface-active lithium salt of the sulfate of the derivative of cis-2-undecyl-5-hydroxy-1,3-dioxane, having a generalized formula 1, in which $n = 11$, $m = 1$, X constitutes the lithium cation Li (85% yield), possesses the following characteristics: empiric formula: $C_{15}H_{29}O_6SLi$; contents, calculated, of C, H, S: 52.31, 8.49, 9.31% by weight, respectively; contents, determined, of C, H, S: 52.30, 8.4, 9.30 % by weight, respectively; melting point (decomposition) 475- 477 K; Krafft point for a 1%-by-weight of aqueous solution: less than 293 K. Surface active cesium salt of the sulfate of the derivative of cis-2-undecyl-5-hydroxy-1,3-dioxane, having a generalized formula 1, in which $n = 11$, $m = 1$, X constitutes the cesium cation Cs (92% mol yield), possesses the following characteristics: empiric formula: $C_{15}H_{29}O_6SCs$; C, H, S- content, calculated: 38.30, 6.21, 6.81 % by weight, respectively; contents, determined: 38.20, 6.20, 6.70% by weight, respectively, melting point (break-down or decomposition) 465-467 K; Krafft point for a 1% by weight aqueous solution is 310 K.

E x a m p l e V.

To a solution of 0.010 kg, i.e. 0.0434 moles of trans-2-nonyl-5-hydroxy-1,3-dioxane in 0.080 dm^3 of dried carbon tetrachloride in $2 \cdot 10^{-3} \text{ dm}^3$ of dried pyridine, there are introduced -

over the course of vigorous agitation, at room temperature - in several batches, 8.3×10^{-3} kg , i.e. 0.0521 moles, of the pyridine sulfur trioxide complex. The thorough mixing continues at the same temperature for a period of 1 hour, while the next thorough agitation is carried out at a temperature of 310 K for a period of 6 to 8 hours. After the evaporation of the solvent, the residue is gradually introduced at room temperature to a suspension of 8.3×10^{-3} kg, i.e. 0.06 moles, of potassium carbonate in 0.12 dm^3 of a mixture of solvents, ethyl alcohol - water (3:1, v/v). After the evaporation of the solvents and the crystallization of the residue from ethyl alcohol, there are furnished 0.0145 kg, i.e. 95 %-mol of surface-active potassium salt of the sulfate of the derivative of trans-2-nonyl-5-hydroxy-1,3-dioxane, having the generalized formula 2, in which $n = 9$, $m = 1$, X constitutes the potassium cation K. Empiric formula: $C_{13}H_{25}O_6SK$; calculated contents of C, H, S: 44.80, 7.23; 9.20 % by weight, respectively; determined contents: 44.7, 7.3, 9.1 % by weight, respectively; melting point (decomposition) 476-478 K; Krafft point for 1% by weight of an aqueous solution: 301 K.

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